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(54) BIOCOMPATIBLE MOULDABLE POLYMERIC MATERIAL

BIOLOGISCH VERTRÄGLICHES FORMBARES POLYMERMATERIAL

MATERIAU POLYMERE MOULABLE BIOCOMPATIBLE

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- **Biomaterials, vol. 8, no. 5, 12 February 1987, Guildford GB, pages 393-396, K.W.M. DAVY: "The mechanical properties of elastomeric poly(alkyl methacrylate)s' cited in the application**

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The file contains technical information submitted after the application was filed and not included in this specification

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Description

The present invention relates to elastomer forming systems which are mouldable at ambient temperatures and which have a low reaction exotherm on setting, to kits comprising the components of such systems and to elastomer materials formed from them. These systems are particularly applicable to techniques for taking impressions of sensitive parts of human and animal bodies and for formation of prostheses. More particularly they are useful in the fabrication of earmoulds and ear impressions for use in hearing aid applications.

Dimensional accuracy of audiological materials, satisfactory handling characteristics and adequate service life are all fundamental requisites of an effective hearing aid fitment programme. Existing commercially available audiological materials have several limitations in so far as they show a high degree of dimensional instability and those whose shrinkage values are within acceptable clinical limits are difficult to handle and expensive. Two-stage earmould materials (eg Molloplast-β) that provide good acoustic seal when used together with an impression material of superior dimensional stability (eg, Otoform AK) are difficult to work with. Venting, surface polishing, bevelling and trimming are difficult to achieve and tubing tends to collapse when mounted within them.

Hard acrylic, which is durable, easily workable in terms of venting and surface polishing, fails to provide good acoustic seal where high gain is required and comfort cannot be ensured due to its texture. Available acrylic based material, cold-cure acrylic poly(methyl -methacrylate), which is used for one stage earmould making suffers from the following limitations:

(i) The setting reaction is highly exothermic, leading to potential discomfort and even damage to the aural tissues;

(ii) High degree of shrinkage (23% by volume for the monomer; 8% by volume for monomer/polymer mix) on setting, leading to dimensional inaccuracy of the impression, with consequences for the accuracy of the final earmould;

(iii) Rigidity, causing red, sore and inflamed ears, resulting from physical irritation by the roughness of the surface of the finished mould;

(iv) Strong fumes from the monomer cause headaches unless a ventilated room is used and

(v) Excessive dryness of the skin is caused when handling the materials (see Bulmer, British Journal of Audiology, 7, 5-8 (1973).

Poly (methyl methacrylate) cold-cure materials have been formally withdrawn from audiological applications in the developed world for such reasons.

EP 0088845 discloses a poly(meth)acrylate composition with reduced curing shrinkage which is useful as a biomedical material. The poly(meth)acrylate is mixed with one or more heterocyclic esters of (meth)acrylic acid, particularly tetrahydrofurfuryl methacrylic acid. In order to produce a hearing aid the composition is mixed, allowed to form a dough and pressed into a plaster mould. Once set the material is ground or polished into the required form.

GB 652057 describes the addition of lower alkyl esters of itaconic acid or styrene to the monomer component of a polymethylmethacrylate and acrylic acid composition in the process of denture manufacture to increase the tensile strength of the resulting material. The moulding composition formed was allowed to form a dough before it was pressed into a mould and heated to produce dentures or artificial teeth.

Although previous studies (eg, Combe and Nolan, Scandinavian Audiology, 18 67-73 (1989) have recognised the need to formulate products that meet with audiological requirements, further investigations into polysulphides and acrylic based materials for impression taking were discouraged due to their reported handling characteristics and lack of stability.

The present invention provides acrylate based materials, particularly homopolymers and copolymers of the higher methacrylates, and their use, inter alia, as audiological and prosthetic moulding materials. These materials provide the advantages of being (i) bio-compatible with tissues, (ii) easily mixed to the required consistency without handling the material, (iii) low in cost, (iv) having a suitable shelf life, (v) much lower in exotherm and shrinkage on setting and (vi) ambient temperature cure.

Previous uses of higher methacrylates have included formation of so-called soft acrylics as soft lining materials for dentures, maxillo-facial prostheses and soft earmould materials (Parker and Braden, Journal of Dentistry (1982) 10, 149-153. There have also been investigations of the properties of cross-linked higher poly -(methacrylates) for testing as ear mould materials (Davy and Braden, Biomaterials (1987) 8, 393-396.

Typical formulations produced by these workers comprised components which would be processed by the dough technique whereby a powder of suspension polymerised copolymer is mixed with liquid monomer to form a dough.

Components used in those formulations comprised:

(i) a copolymer powder containing an initiator;
(ii) monomer liquid;
(iii) plasticizer;
(iv) cross-linking agent;
(v) activator and
(vi) anti-tack agent (which also reduces internal friction in extrusion).

Studies have consistently demonstrated that the most accurate process for making earmoulds at the present time is the one-stage approach (Combe and Nolan, Scandinavian Audiology, (1989) 18, 67-73), but that the weakest component of this approach is material. Audiological use requires sufficient fluidity to enable the materials to be loaded into a standard audiological syringe and then injected into the external auditory meatus in the manner of the standard audiological clinical 30 technique. The use of higher methacrylates (ie:C_7 to C_{20} esters) by these workers was found to result in requirement for temperatures of the order of 80°C to 100°C in order to cure; clearly unsuited to the one-stage method.

Similarly it is noted that the currently available dimensionally stable silicone based impression materials for a two-stage earmould process introduce a problem in wax-dipping, have set backs of poor dimensional stability and have low resistance to tearing. It is therefore necessary to develop new criteria that would be a guide to development of suitable clinical material which itself can be used as a one-stage earmould material and yet would still be suitable for ear impression material for the two-stage earmould process.

The following set of desirable properties are considered appropriate in developing a clinical product suitable for audiological use:

(i) Biocompatibilty with aural tissues: the monomer system should be non-toxic, non-irritant and the setting reaction should have a low exotherm;

(ii) Suitable handling characteristics: when the powder and monomer are mixed the consistency of the dough formed should be such as to enable easy syringing into the ear using commercially available syringes with a sufficient working time of 2 to 3 minutes and a setting time of 4 to 7 minutes;

(iii) Dimensional stability: shrinkage should be minimal, not more than 2 to 3% linear; and dimensional stability over different temperature and humidity ranges as might be encountered in various applicable ambients (eg, tropical use);

(iv) Suitable mechanical or rheological properties: the set material should be elastomeric with freedom from permanent deformation; resilience; adequate strength to prevent tearing or breakage on removal from the ear or during processing such as core boring, insertion of sound tubes, venting; satisfactory consistency and texture to provide comfort; ease of use with the minimum of equipment (preferably no drilling); compatibility with wax if used as an impression material in the two-stage process and with available tubing material generally.

(v) Durability: the components should have adequate shelf life for the requirements of storage and distribution and the final product should have an acceptably high service life;

(vi) Function: the final earmould should have potential for handling high acoustic gain required for users of high powered hearing aids;

(vii) Cosmetics: the final earmould material should be aesthetically pleasing and have no offensive odour;

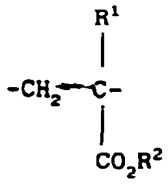
(viii) Management: the material should be capable of being easily cleaned with ordinary water and washing up liquid.

It is an object of the present invention to provide mouldable curable polymer/monomer systems and biocompatible polymeric materials produced from them. It is a further object of the present invention to provide such systems and materials produced from them which are suitable for either audiological or prosthetic uses or both, particularly for use in the one-stage and/or two-stage earmould material preparation and having improved properties in at least some of the respects outlined in the list (i) to (viii) above over the known materials. The polymer /monomer system is based upon use of a higher (C_7 to C_{20} alkyl) acrylate or methacrylate based monomer component which is capable of curing at ambient temperatures with an acceptable lower exotherm. The preferred compositions and elastomers of the inven-

tion are improved in all respects (i) to (viii).

The present invention provides a mouldable curable polymer/monomer system comprising a polymer component, a monomer component and a plasticizer characterised in that:

(a) the polymer component comprises one or more polymers of molecular weight of from 300,000 to 2,000,000 which each comprise repeat units of one or both of general formula I and general formula II:



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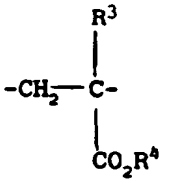
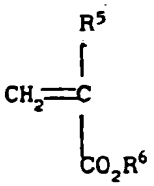


II

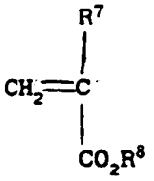
wherein R^1 and R^3 are the same or different and are selected from H or methyl and R^2 and R^4 are the same or different and are selected from alkyl groups containing from 1 to 6 carbon atoms, but wherein either R^3 is different to R^1 or R^4 is different to R^2 and;

(b) the monomer component comprises 80 to 99 % weight of a monomer of general formula III:



III

wherein R^5 is H or methyl and R^6 is an alkyl group of from 7 to 20 carbon atoms;
together with from 1 to 20% weight of a monomer of formula IV:



IV

wherein R^7 is H or methyl and R^8 is H or an alkyl group containing from 1 to 3 carbons.

Preferably the ratio of the polymer component to the total of the monomer component and the plasticizer is from 5:1 to 1:2 weight:weight and the ratio of the monomer to the plasticizer is from 85:15 to 35:65 weight:weight. More preferably the polymer component is provided in a ratio of from 3:1 to 1:1, more preferably 5:2, weight:weight to the total weight of the monomer and the plasticizer.

The polymer may be a homopolymer or a copolymer but for audiological use it preferably comprises random copolymers of C_1 to C_6 alkyl esters of methacrylic acid, for example ethyl/methyl- or n-butyl/ethylmethacrylate copolymers. The ratio of the ester components in the copolymer may vary from 10:90 to 90:10, more preferably from 20:80 to 80:20 and particularly from 30:70 to 70:30 weight to weight, eg. 60:40. Most preferably the polymer component comprises a random copolymer of n-butyl/ethyl methacrylates corresponding to a copolymer comprising repeats of formula I wherein R^1 is methyl and R^2 is n-butyl and repeats of formula II wherein R^3 is methyl and R^4 is ethyl.

Preferably the monomer component monomer of formula III has H as R^5 and an alkyl group of from C_8 to C_{16} as R^6; more preferably R^6 is an alkyl group of C_{13}. Conveniently the compound of formula III is provided as an isomeric mixture of such monomers having on average 13 carbons in R^6 as sold under the tradename 'Methacryl Ester 13' by Rohm Chemie.

Preferably the monomer of formula IV comprises R^7 as methyl and R^8 as H. Preferably the monomer of formula

III comprises 90 to 95 % by weight of the monomer component with the monomer of formula IV providing the balance.

Typical suitable platicizers are fumarates, maleates or itaconates, for example, di-2-ethylhexyl fumarate, di-2-ethylhexyl maleate or di-2-ethylhexyl itaconate, although other suitable plasticizers will occur to those skilled in the art.

Preferably for storage the monomer and plasticizer are combined as a single component, the plasticizer comprising accordingly from 15 to 65 % weight of that combined component, thus allowing facile mixing of the polymer and combined components when required. Preferably the combined monomer/plasticizer component comprises from 45 to 75 % weight of a monomer of formula III, from 1 to 5 % weight of a monomer of formula IV and correspondingly from 54 to 20 % weight plasticizer content.

In order to enable satisfactory curing on mixing of the polymer, monomer and plasticizer components a cross-linking agent, an activator or photoinitiator, and optionally an anti-tack agent will be added to the components of the polymer/monomer system. Conveniently the anti-tack and cross-linking components are provided in the monomer component and the activator or photo-initiator will be provided in either the monomer or polymer component. Such combinations allow stable storage until dough is required. Suitable amounts of these additives will occur to those skilled in the art but typically will be eg: 0.5 to 2 % wt crosslinker, 0.2 to 6% photoinitiator or 1 to 6 % wt activator , all based on weight of the monomer of formula III as 100%.

Typical suitable cross-linking agents include eg, ethylene glycol dimethylacrylate, triethylene glycol dimethacrylate and/or tetraethylene glycol methacrylate. Typical suitable activators include eg, N,N-dimethyl-p-toluidine, N,N-dihydroxyethyl-p-toluidine and/or lauryl mercaptan while suitable photoinitiators include eg. anthraquinone or N,N-dimethyl-p-toluidine. Typical suitable anti-tack agents include silicone oil, zinc stearate and/or liquid paraffin.

The addition to the polymer component of 1 % weight of an activating peroxide, eg. benzoyl peroxide as an activating compound further reduces the setting time of dough produced on mixing the two components. A suitable form of this component is provided in Lucidol CH50, a benzoyl peroxide/dicyclohexyl phthalate mix containing 50 % weight of peroxide thus requiring it to be added as 2 % weight of the polymer. Addition of such peroxide reduces the ambient temperature curing time of these systems from 10 minutes to 5 minutes.

Preferably the polymer component is produced as a powder to enhance it's miscibility with the liquid monomer system. Preferred examples of the polymer component of the system of the invention include those comprising n-butyl methacrylate:ethyl methacrylate random copolymer of ratio 70:30 to 40:60 (n-butyl:ethyl), the most preferred ratio being 60:40. Such a copolymer is available from Bonar Polymers Ltd, County Durham, UK, as are a variety of others.

Thus, in a preferred embodiment, the invention provides an audiological earmould or earpiece forming composition comprising a system as described above, in which the polymer component comprises an n-butylmethacrylate/methylmethacrylate random copolymer in a ratio of from 70:30 to 40:60 weight by weight, and which further includes a cross-linking agent, an activator or photoinitiator and optionally an anti-tack agent.

A preferred system of the invention uses said 60:40, n-butyl methacrylate: ethyl methacrylate random copolymer as the polymer component and a monomer/plasticizer component comprised of Methacrylate Ester 13 and methacrylic acid mixed with di-2-ethylhexyl maleate, ethylene glycol dimethacrylate and N,N dimethyl-p-toluidine.

It will be appreciated that the term 'system' used throughout this specification refers to a combination of components necessary for production of the mouldable material and subsequent elastomer of the present invention. Thus the term 'system' covers such components as presented together in a form suitable for use in preparing a mouldable material or elastomer of the present invention, or as dough itself.

For example the system may be provided as a kit in which the polymer and monomer components are supplied in a form which prevents them from reacting with each other until desired. Such form may be achieved by keeping both components in separate compartments while including the other active ingredients such as initiators and crosslinkers with one or other of them or in a further separate compartment.

A method for forming a biocompatible curable mouldable dough comprising mixing the components of a system as described above, forms a further aspect of the invention..

Alternatively, the polymer and monomer components may be supplied in premixed form and the other active ingredients may be provided in a separate compartment or container within the kit for admixture with them when curing is desired. Some photoinitiator cured systems may be provided in completely mixed form in light sealed packages. The precise form most suited to a particular use will be apparent to a man skilled in the art from his selected component's reactivity.

Similarly, the selection of components for a given kit will be influenced by the particular intended use. For use where moulding involves contact of the uncured dough with more delicate parts of the body it will be desirable to keep any exotherm down to a minimum level, notwithstanding the generally low exotherms provided by the systems of the present invention. Such minimal exotherms may be provided, without critical loss of curing rate, by using amounts of monomer IV that are below 5% by weight of the monomer component as a whole.

Furthermore, where tissues are more prone to react to acrylic acid this should be avoided in favour of methacrylic acid for use as said monomer IV. It is known that methacrylic acid itself has some toxic effects and thus for use in earmoulding the preferred level of this component is 10%, more preferably 5% by weight of the monomer component

in total.

Thus the invention further provides a method for forming an impression of a part of a human or animal body, such as part of the meatus of a human ear, comprising use of a dough formed by mixing the components of the above-mentioned system together. Alternatively, the impression may be used to form a prosthesis.

Thus in a preferred embodiment, the invention provides a method for forming an audiological earmould or earpiece comprising injecting a dough formed by mixing the components of the above-mentioned system together, into a meatus of a human ear and curing.

Elastomers comprising a system as described above which has been mixed together and polymerised, for example by curing, forms a further aspect of the invention. Suitably the curing is effected at between ambient temperature and body temperature. The invention yet further provides earmoulds or earpieces as well as prosthesis comprising the elastomers.

The polymer/monomer systems of the invention and their application to audiological earmould use will now be illustrated, by way of exemplification only, with reference to the following Examples.

EXAMPLE 1.

Two monomer/plasticizer/cross-linking agent/activator component mixtures (A) and (B) were produced having the following compositions in parts by weight:

Mixture:	(A)	(B)
Component:		
Methacryl Ester 13*	75	55
Methacrylic acid*	5	5
Di-2-ethylhexyl maleate+	20	40
Ethylene glycol dimethacrylate^	0.5	0.5
N,N dimethyl-p-toluidine^	2.5	2.5

*=monomers;
+=plasticizer;
^=cross-linker and activator respectively.

The mixtures were çseparately mixed with powdered 60:40 n-butyl -methacrylate:ethylmethacrylate copolymer (Bonar polymers) in the ratio of 5:2 powder to monomer mixture weight by weight. Both doughs proved to be easily syringeable in the ear and were easily removed at the onset of polymerization. The particle size range of the copolymer component used was approximately from 5 to 85 μW (microns) diameter.

EXAMPLE 2.

A monomer/plasticizer/cross-linking agent/activator/ anti-tack agent component was formulated comprising the following composition as indicated in millilitres:

Composition:	ml
Methacryl Ester 13 (Rohm Chemie)	27.5
Methacrylic acid	2.5
di-2-ethylhexylmaleate	20.0
Ethylene glycol dimethacrylate	0.25
N,N-dimethyl-p-toluidine	1.25
Liquid paraffin*	11.6

*=anti-tack agent

The above described liquid composition was mixed with 60:40 (Bonar) n-butylmethacrylate:ethylmethacrylate random copolymer in the ratio of 2.5 grams powdered copolymer per ml of monomer liquid. The dough produced proved to be easily syringeable into the ear and was readily removed at the onset of polymerization.

BIO-COMPATABILITY STUDIES.

The material of Example 2 was syringed into the ears of volunteers where it was worn for a period of approximately 5 hours. The volunteers comprised six hearing impaired subjects and two normally hearing adults. No toxic or irritant side effects were seen on the aural tissues of any of the volunteers and the two adults reported that the exotherm on curing was minimal.

Mixing and syringing took of the order of 2 minutes and setting took 5 minutes at ear temperature. When the material was fully mixed using a bowl and a spatula it became cohesive to the spatula and could easily be loaded into a syringe from it.

It was observed that the cured material finely reproduced the surface of the meatal skin and was elastomeric, resilient, easy to cut and core bore and was highly resistant to tearing. The product polymer has a shiny surface and thus does not require any varnishing. Studies on its interaction with other materials show that it does not discolour available pre-bent tubing after eight weeks observation and said tubing may be stabilised in the cured polymer without the use of glue; vents made in the cured material were noted to remain open unlike other soft earmould materials.

ACOUSTIC SUITABILITY.

As can be seen from Tables II and III, the acoustic attenuation of the material of Example 2 compares favourably with known earmould material. The shrinkage of this C_{13} based monomer material was only 8 % vol/vol compared to 23 % for mainly methylmethacrylate based materials; this is equivalent to only 3 % linear shrinkage. Calculations based upon the amount of material used per earmould indicate that only 1 % linear shrinkage might be expected.

ATTENUATION VALUES.

The acoustic attenuation values obtained with the six hearing impaired subjects using earmoulds produced with the material of Example 2 are shown in Table II. Subject details are given in Table I.

TABLE I

Details of subjects trialing earmoulding using system of Example 2.				
Subject 01:	male:	14yrs:	phonak PPC-LA hearing aid:	av Pta(R) 105
02:	male:	15yrs:	(RTM) PPC-2 :	102
03:	female:	12yrs:	PPC-LA :	112
04:	male:	11yrs:	PPC-LA :	103
05:	male:	13yrs:	PPC-LA :	106
06:	female:	29yrs:	PPC-LA :	105

TABLE II

Attenuation values (dB) obtained from soft one-stage earmoulds made from the system of Example II.									
Subject	Frequency (KHz)								
	0.2	0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0
01	56.3	63.4	63.8	64.3	63.2	62.9	63.7	61.2	63.6
02	59.9	63.4	65.5	64.9	65.4	65.0	66.6	64.5	63.4
03	60.1	63.1	63.6	63.7	64.3	62.0	57.7	57.8	68.8
04	60.0	63.2	63.4	63.2	61.1	57.7	57.2	58.2	58.6
05	59.8	62.6	62.6	62.4	59.3	57.0	54.8	52.6	56.2
06	60.1	63.3	63.9	63.7	64.6	65.8	68.4	72.3	70.3
MEAN	59.4	63.2	63.8	63.7	63.0	61.7	61.4	61.1	63.5

TABLE III

Analysis of feedback of one-stage earmoulds made from the system of Example II.			
No. of Earmoulds	No Feedback Maxvol ≥ NORVOL	Feedback Maxvol < NORVOL	% with Feedback (out of 6)
6	6	0	0.0
MAXVOL = MAXIMIUM VOLUME SETTING NORVOL = NORMAL/USER'S VOLUME SETTING Using aids shown in Table I			

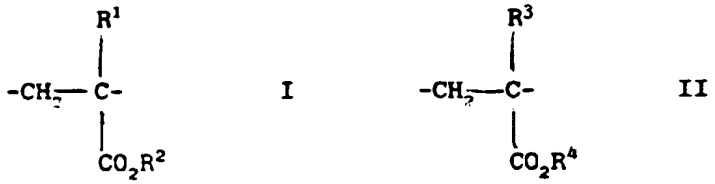
The elastomeric earmoulds were core bored and fitted with sound tubes for these evaluations. Examples were highly compatible with currently available PVC tubing and this remained stable within the earmould without glue and without hardening with age. The elastic modulus of the material was such that body temperature caused it to be softer in contact with the ear than on its outer surface. The earmoulds provided ease of insertion and removal, having elastomeric and resilient properties well suited for this purpose. Washing in ordinary warm/cold water and standard washing up liquid caused no observable deterioration.

The systems of the present invention are suitable for further uses; particularly such as provision of soft lining material for the good fitting of dentures and in the provision of maxillo-facial prostheses. It will be realised that many other uses requiring bio-compatible materials that are mouldable and curable in situ yet which do not provide exotherm or toxicity problems may be found for the materials by correct selection of the components. For example, if curing inside a human body one might use methacrylic rather than acrylic acids for toxicity reasons, as stated above. Where the inherent elastomeric and biocompatibility properties of the moulded elastomer material are desired but there is reduced requirement to avoid exotherm or toxicity with the moulding stage, ie. due to contact with uncured dough, increased amounts of methacrylic acid or acrylic acid may be used. Thus prostheses may be produced outside the body with varying properties and may be cured after moulding away from said body.

Claims

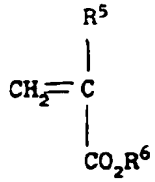
1. A mouldable curable polymer/monomer system comprising a polymer component, a monomer component and a plasticizer characterised in that:

   (a) the polymer component comprises one or more polymers of molecular weight of from 300,000 to 2,000,000 which each comprise repeat units of one or both of general formula I and general formula II:



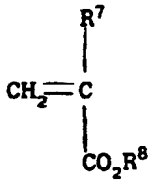
   wherein R^1 and R^3 are the same or different and are selected from H or methyl and R^2 and R^4 are the same or different and are selected from alkyl groups containing from 1 to 6 carbon atoms, wherein either R^3 is different to R^1 or R^4 is different to R^2 and;

   (b) the monomer component comprises 80 to 99 % weight of a monomer of general formula III:



III

wherein R^5 is H or methyl and R^6 is an alkyl group of from 7 to 20 carbon atoms; together with from 1 to 20% weight of a monomer of formula IV:



IV

wherein R^7 is H or methyl and R^8 is selected from H and an alkyl group containing from 1 to 3 carbons.

2. A system according to Claim 1 wherein the ratio of the polymer component to one total of the monomer component and the plasticizer is from 5:1 to 1:2 weight:weight and the ratio of the monomer to the plasticizer is from 85:15 to 35:65 weight:weight.

3. A system according to Claim 2 wherein the polymer component is provided in a ratio of from 3:1 to 1:1 weight: weight to the total monomer component and the plasticizer,

4. A system according to Claim 3 wherein the polymer component is provided in a ratio of 5:2 weight:weight to the total weight of the monomer and the plasticizer.

5. A system according to any one of the preceding claims wherein the polymer component comprises a random copolymer of C_1 to C_6 alkyl esters of methacrylic acid.

6. A system according to any one of the preceding claims wherein the polymer component comprises an ethylmethacrylate/methylmethacrylate random copolymer or a n-butylmethacrylate/ethylmethacrylate random copolymer.

7. A system according to Claim 6 wherein the polymer component comprises a copolymer of n-butylmethacrylate and ethylmethacrylate in the ratio 70:30 to 40:60 weight to weight.

8. A system according to Claim 1 wherein the monomer component monomer of formula III has H as R^5 and an alkyl group of from C_8 to C_{16} as R^6.

9. A system according to Claim 8 wherein R^6 is an alkyl group of C_{13}.

10. A system according to Claim 9 wherein the monomer of formula III is provided in an isomeric mixture of such monomers having on average 13 carbons in R^6.

11. A system according to Claim 1 wherein the monomer of formula IV is methacrylic acid.

12. A system according to Claim 11 wherein the monomer of formula III comprises 90 to 95 % by weight of the monomer component with the monomer of formula IV providing the balance.

13. A system as claimed in any one of the preceding claims wherein the plasticizer comprises a fumarate, a maleate or an itaconate.

14. A system as claimed in claim 13 wherein the plasticizer comprises di-2-ethylhexyl fumarate, di-2-ethylhexyl maleate or di-2-ethylhexyl itaconate.

15. A system as claimed in any one of the preceding claims further comprising a cross-linking agent and an activator or photoinitiator.

16. A system as claimed in any one of the preceding claims further comprising an anti-tack agent.

17. A biocompatible impression taking composition comprising a system according to any one of Claims 1 to 16 wherein the components of the system have been mixed together.

18. An audiological earmould or earpiece forming composition comprising a system according to Claim 7 which further includes a cross-linking agent, an activator or photoinitiator and optionally an anti-tack agent.

19. A method for forming a biocompatible curable mouldable dough comprising mixing the components of a system as claimed in any one of Claims 1 to 16.

20. A method for forming an impression of a part of a human or animal body comprising use of a dough as provided by the method of Claim 17.

21. A method as claimed in Claim 20 wherein said impression comprises part of the meatus of a human ear.

22. A method for forming an audiological earmould or earpiece comprising injecting a dough as provided by the method of Claim 17 into the meatus of a human ear and curing.

23. A method as claimed in Claim 20 wherein the impression is used to form a prosthesis.

24. An elastomer comprising a system as claimed in any one of Claims 1 to 16 that has been mixed together and polymerised.

25. An elastomer comprising a system as claimed in Claim 15 wherein the system is cured for polymerisation.

26. An elastomer as claimed in Claim 25 wherein the system is cured at between ambient and body temperature.

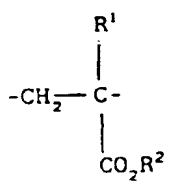
27. An earmould or earpiece comprising an elastomer as claimed in any one of Claims 24 to 26.

28. A prosthesis comprising an elastomer as claimed in any one of Claims 24 to 26.

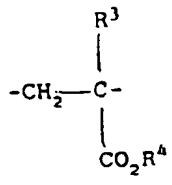
Revendications

1. Système polymère/monomère durcissable moulable comprenant un composant polymère, un composant monomère et un plastifiant, caractérisé en ce que :

(a) le composant polymère comprend un ou plusieurs polymères de poids moléculaire allant de 300 000 à 2 000 000, dont chacun contient des motifs répétés de formule générale I ou de formule générale II ou des deux :



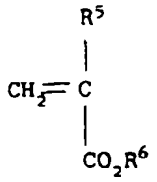
I



II

où R^1 et R^3 sont identiques ou différents et sont choisis entre l'hydrogène et un groupe méthyle et R^2 et R^4 sont identiques ou différents et sont choisis entre des groupes alkyle contenant 1 à 6 atomes de carbone,

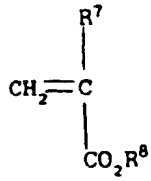
R^3 étant différent de R^1 ou bien R^4 étant différent de R^2 et ;
(b) le composant monomère comprend 80 à 99 % en poids d'un monomère de formule générale III :



III

dans laquelle R^5 est de l'hydrogène ou un groupe méthyle et R^6 est un groupe alkyle ayant 7 à 20 atomes de carbone ;

conjointement avec 1 à 20% en poids d'un monomère de formule IV :



IV

dans laquelle R^7 est de l'hydrogène ou un groupe méthyle et R^8 est choisi entre l'hydrogène et un groupe alkyle contenant 1 à 3 atomes de carbone.

2. Système suivant la revendication 1, dans lequel le rapport en poids : poids du composant polymère au total du composant monomère et au plastifiant va de 5 : 1 à 1 : 2 et le rapport en poids : poids du monomère au plastifiant va de 85 : 15 à 35 : 65.

3. Système suivant la revendication 2, dans lequel le rapport en poids : poids du composant polymère au total du composant monomère et du plastifiant va de 3 : 1 à 1 : 1.

4. Système suivant la revendication 3, dans lequel le rapport en poids : poids du composant polymère au poids total du monomère et du plastifiant est égal à 5 : 2.

5. Système suivant l'une quelconque des revendications précédentes, dans lequel le composant polymère comprend un copolymère statistique d'esters alkyliques en C_1 à C_6 de l'acide méthacrylique.

6. Système suivant l'une quelconque des revendications précédentes, dans lequel le composant polymère comprend un copolymère statistique méthacrylate d'éthyle/méthacrylate de méthyle ou un copolymère statistique méthacrylate de n-butyle/méthacrylate d'éthyle.

7. Système suivant la revendication 6, dans lequel le composant polymère comprend un copolymère de méthacrylate de n-butyle et de méthacrylate d'éthyle dans le rapport en poids : poids de 70 : 30 à 40 : 60.

8. Système suivant la revendication 1, dans lequel R^5 est de l'hydrogène et R^6 est un groupe alkyle en Ce à C_{16} dans le monomère de formule III du composant monomère.

9. Système suivant la revendication 8, dans lequel R^6 est un groupe alkyle en C_{13}.

10. Système suivant la revendication 9, dans lequel le monomère de formule III est présent dans un mélange isomérique de tels monomères dans lesquels R^6 a en moyenne 13 atomes de carbone.

11. Système suivant la revendication 1, dans lequel le monomère de formule IV est l'acide méthacrylique.

12. Système suivant la revendication 1, dans lequel le monomère de formule III constitue 90 à 95% en poids du composant monomère, le monomère de formule IV représentant le reste.

13. Système suivant l'une quelconque des revendications précédentes, dans lequel le plastifiant comprend un fumarate, un maléate ou un itaconate.

14. Système suivant la revendication 13, dans lequel le plastifiant comprend le fumarate de di-2-éthylhexyle, le maléate de di-2-éthylhexyle ou l'itaconate de di-2-éthylhexyle.

15. Système suivant l'une quelconque des revendications précédentes, comprenant en outre un agent de réticulation et un activateur ou photoinitiateur.

16. Système suivant l'une quelconque des revendications précédentes, comprenant en outre un agent anti-adhésif.

17. Composition biocompatible pour la prise d'empreintes, comprenant un système suivant l'une quelconque des revendications 1 à 16, dont les composants ont été mélangés ensemble.

18. Composition destinée à former un moulage auriculaire ou embout audiologique, comprenant un système suivant la revendication 7 qui contient en outre un agent de réticulation, un activateur ou photoinitiateur et facultativement un agent anti-adhésif.

19. Procédé pour former une pâte moulable durcissable biocompatible, qui consiste à mélanger les composants d'un système suivant l'une quelconque des revendications 1 à 16.

20. Procédé pour former une empreinte d'une partie d'un corps humain ou animal, comprenant l'utilisation d'une pâte telle qu'obtenue par le procédé suivant la revendication 17.

21. Procédé suivant la revendication 20, dans lequel l'empreinte en question comprend une partie du conduit auditif d'une oreille humaine.

22. Procédé pour former un moulage auriculaire ou un embout audiologique, comprenant l'injection d'une pâte telle qu'obtenue par le procédé suivant la revendication 17 dans le conduit auditif d'une oreille humaine et le durcissement de la pâte.

23. Procédé suivant la revendication 20, dans lequel l'empreinte est utilisée pour former une prothèse.

24. Elastomère comprenant un système suivant l'une quelconque des revendications 1 à 16, qui a été malaxé et polymérisé.

25. Elastomère comprenant un système suivant la revendication 15, qui est durci en vue de sa polymérisation.

26. Elastomère suivant la revendication 25, dans lequel le système est durci entre la température ambiante et la température du corps.

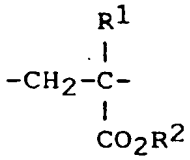
27. Moulage ou embout auriculaire comprenant un élastomère suivant l'une quelconque des revendications 24 à 26.

28. Prothèse comprenant un élastomère suivant l'une quelconque des revendications 24 à 26.

Patentansprüche

1. Formbares, härtbares Polymer/Monomer-System, das eine Polymer-Komponente, eine Monomer-Komponente und einen Weichmacher enthält, welches dadurch gekennzeichnet ist, daß:

   (a) die Polymer-Komponente ein oder mehrere Polymere mit einem Molekulargewicht von 300 000 bis 2 000 000 enthält, die jeweils Wiederholungseinheiten der allgemeinen Formel I und/oder der allgemeinen Formel II aufweisen:



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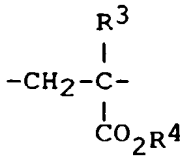
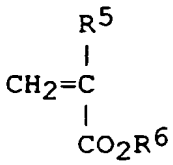


II

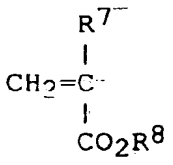
wobei R^1 und R^3 gleich oder voneinander verschieden sind und unter H oder Methyl ausgewählt sind und R^2 und R^4 gleich oder voneinander verschieden sind und unter Alkyl-Gruppen, die 1 bis 6 Kohlenstoffatome enthalten, ausgewählt sind, wobei entweder R^3 sich von R^1 unterscheidet oder R^4 sich von R^2 unterscheidet, und

(b) die Monomer-Komponente 80 bis 99 Gew.-% eines Monomers der allgemeinen Formel III enthält:



III

wobei R^5 H oder Methyl und R^6 eine Alkylgruppe mit 7 bis 20 Kohlenstoffatomen ist,
und zwar zusammen mit 1 bis 20 Gew.-% eines Monomers der Formel IV:



IV

wobei R^7 H oder Methyl ist und R^8 unter H oder einer 1 bis 3 Kohlenstoffatome enthaltenden Alkylgruppe ausgewählt ist.

2. System nach Anspruch 1, wobei das Gewichtsverhältnis Polymer-Komponente zu Monomer-Komponente und Weichmacher insgesamt 5:1 bis 1:2 beträgt und das Gewichtsverhältnis Monomer zu Weichmacher 85:15 bis 35:65 beträgt.

3. System nach Anspruch 2, wobei die Polymer-Komponente im Gewichtsverhältnis 3:1 bis 1:1 zur gesamten Monomer-Komponente und dem Weichmacher bereitgestellt wird.

4. System nach Anspruch 3, wobei die Polymer-Komponente im Gewichtsverhältnis 5:2 zum Gesamtgewicht des Monomers und des Weichmachers bereitgestellt wird.

5. System nach einem der vorhergehenden Ansprüche, wobei die Polymer-Komponente ein statistisches Copolymer aus C_1-C_6-Alkylestern von Methacrylsäure enthält.

6. System nach einem der vorhergehenden Ansprüche, wobei die Polymer-Komponente ein statistisches Ethylmethacrylat/Methylmethacrylat-Copolymer oder ein statistisches n-Butylmethacrylat/Ethylmethacrylat-Copolymer enthält.

7. System nach Anspruch 6, wobei die Polymer-Komponente ein Copolymer aus n-Butylmethacrylat und Ethylmethacrylat im Gewichtsverhältnis 70:30 bis 40:60 enthält.

8. System nach Anspruch 1, wobei bei dem Monomer der Formel III der Monomer-Komponente R^5 H und R^6 eine

C_8-C_{16}-Alkyl-Gruppe ist.

9. System nach Anspruch 8, wobei R^6 eine C_{13}-Alkylgruppe ist.

10. System nach Anspruch 9, wobei das Monomer der Formel III in Form eines Isomerengemisches aus Monomeren mit durchschnittlich 13 Kohlenstoffatomen für R^6 bereitgestellt wird.

11. System nach Anspruch 1, wobei das Monomer der Formel IV Methacrylsäure ist.

12. System nach Anspruch 11, wobei das Monomer der Formel III 90 bis 95 Gew.-% der Monomer-Komponente ausmacht und das Monomer der Formel IV den Rest bildet.

13. System nach einem der vorhergehenden Ansprüche, wobei der Weichmacher ein Fumarat, ein Maleat oder ein Itaconat umfaßt.

14. System nach Anspruch 13, wobei der Weichmacher Di-2-ethylhexylfumarat, Di-2-ethylhexylmaleat oder Di-2-ethylhexylitaconat umfaßt.

15. System nach einem der vorhergehenden Ansprüche, das außerdem ein Vernetzungsmittel und einen Aktivator oder Photoinitiator enthält.

16. System nach einem der vorhergehenden Ansprüche, das außerdem ein Antiklebrigkeitsmittel enthält.

17. Biologisch verträgliche Zusammensetzung zur Abnahme von Nachbildungen, die ein System nach einem der Ansprüche 1 bis 16 enthält, wobei die Komponenten des Systems miteinander vermischt worden sind.

18. Zusammensetzung zur Herstellung einer audiologischen Ohrnachformung oder eines Ohrstückes, die ein System nach Anspruch 7 enthält, das außerdem ein Vernetzungsmittel, einen Aktivator oder Photoinitiator und gegebenenfalls ein Antiklebrigkeitsmittel enthält.

19. Verfahren zur Herstellung eines biologisch verträglichen, härtbaren, formbaren Teigs, bei dem die Komponenten eines Systems nach einem der Ansprüche 1 bis 16 vermischt werden.

20. Verfahren zur Herstellung einer Nachbildung eines Teils eines menschlichen oder tierischen Körpers, das die Verwendung eines nach dem Verfahren von Anspruch 17 bereitgestellten Teiges umfaßt.

21. Verfahren nach Anspruch 20, wobei die Nachbildung einen Teil des Gehörganges eines menschlichen Ohres umfaßt.

22. Verfahren zur Herstellung einer audiologischen Ohrnachformung oder eines Ohrstücks, bei dem ein nach dem Verfahren von Anspruch 17 bereitgestellter Teig in den Gehörgang eines menschlichen Ohrs injiziert und gehärtet wird.

23. Verfahren nach Anspruch 20, wobei die Nachbildung zur Herstellung einer Prothese verwendet wird.

24. Elastomer, das ein System nach einem der Ansprüche 1 bis 16, das zusammengemischt und polymerisiert wurde, enthält.

25. Elastomer, das ein System nach Anspruch 15 enthält, wobei das System zur Polymerisation gehärtet wird.

26. Elastomer nach Anspruch 25, wobei das System zwischen der Raum- und der Körpertemperatur gehärtet wird.

27. Ohrnachformung oder Ohrstück, die/das ein Elastomer nach einem der Ansprüche 24 bis 26 enthält.

28. Prothese, die ein Elastomer nach einem der Ansprüche 24 bis 26 enthält.